

Supplementary Materials: Zr-Based MOF-808 as Meerwein–Ponndorf–Verley Reduction Catalyst for Challenging Carbonyl Compounds

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1. Characterization

1.1. Powder X-Ray Diffraction

Powder X-ray diffractograms were routinely collected on a STOE STADI COMBI P diffractometer in High-Throughput mode, equipped with an image plate detector using CuK α radiation ($\lambda = 1.54056 \text{ \AA}$). Diffractograms of the materials are shown in Figure S1.

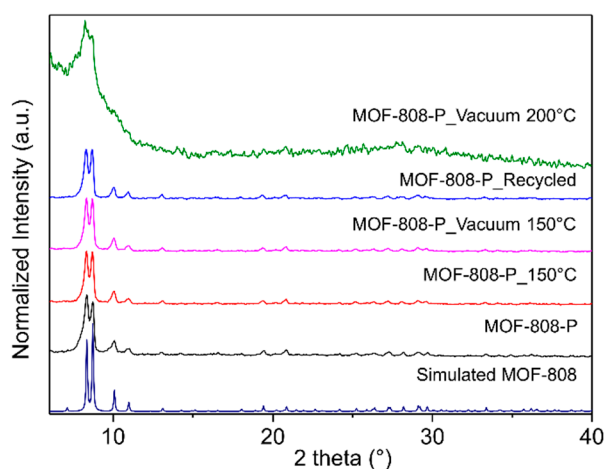


Figure S1. Powder X-ray diffractograms of MOF-808-P: simulated MOF-808 pattern, as synthesized MOF-808-P, activated at 150 °C and 200 °C for 16 h and recycled after reaction.

1.2. Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) images were obtained using a JEOL SEM (JSM-6010LV).

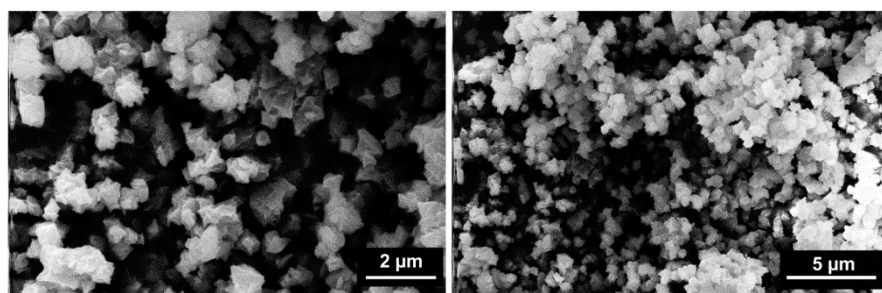


Figure S2. SEM micrograph of MOF-808-P.

1.3. Thermogravimetric Analysis

MOF-808-P was analyzed by Thermogravimetric Analysis (TGA) under a stream of O₂-gas using a Universal V4.5A TA Instrument running from room temperature to 650 °C with a scan rate of 5 °C/min. Weight losses at about 190 °C, 270 °C, and 475 °C can most probably be attributed to respectively solvent (DMF), formate, and 1,3,5-benzenetricarboxylic acid (BTC)-linker loss.

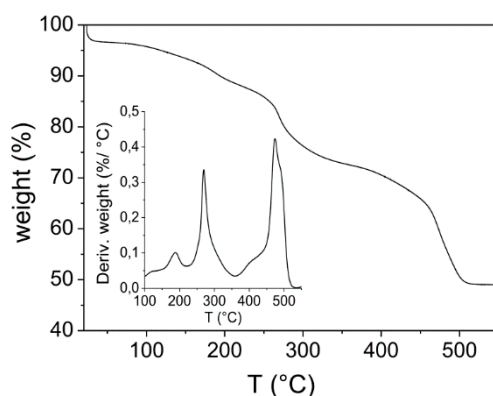


Figure S3. Thermogravimetric Analysis.

1.4. CD₃CN Chemisorption

Sorption with deuterated acetonitrile (CD₃CN) (Figure S4) indicated a larger ratio of chemisorbed molecules on Lewis acid sites to physisorbed molecules (vibration frequency at 2297 cm⁻¹ and 2265 cm⁻¹, respectively) for MOF-808-P compared to UiO-66 after activation at 150 °C. A large fraction of the CD₃CN molecules on the Lewis acid sites of MOF-808-P stay chemisorbed upon desorption under vacuum with increasing temperature to 150 °C, indicating a high acid strength.

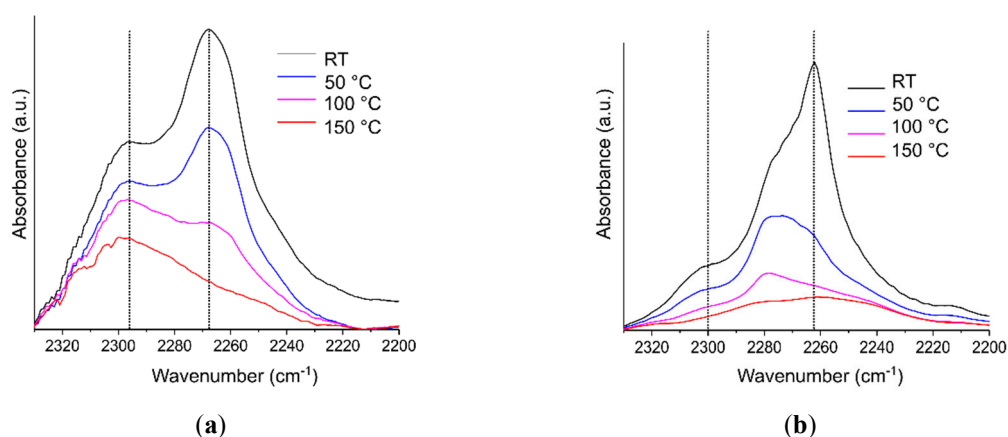


Figure S4. Normalized FTIR spectra of CD₃CN chemisorption on MOF-808-P (a) and UiO-66 (b) at 10 mbar (RT) and desorption under vacuum at increasing temperature.

1.5. Elemental Analysis

Inductively Coupled Plasma (ICP)–Atomic Emission Spectra (AES) were recorded on a Varian 720-ES. Sample breakdown was performed in 0.5 mL aqua regia (1:3 HNO₃:HCl) and 3 mL HF (40 %) for 1 h at 100 °C. The HF-solution was neutralized with excess H₃BO₃ 99.99 % and the spectral signal was compared to Zirconium Standard (TraceCERT, 1000 mg/L Zr in HNO₃; HF Sigma-Aldrich Cat. N° 73574).

Table S1. Theoretical molecular formula and Zr-percentage compared to ICP-AES analysis of self-synthesized MOF-808-P activated at 150 °C (16 h).

Entry	Material	Molecular Formula	wt % Zr
1	MOF-808 [32]	[Zr ₆ O ₄ (OH) ₄](HCOO) ₆ [C ₆ H ₃ (COO) ₃] ₂	40.15
2	MOF-808-P.2H ₂ O [33]	[Zr ₆ O ₅ (OH) ₃](HCOO) ₅ [C ₆ H ₃ (COO) ₃] ₂ (H ₂ O) ₂	40.43
3	MOF-808-P.2DMF [33]	[Zr ₆ O ₅ (OH) ₃](HCOO) ₅ [C ₆ H ₃ (COO) ₃] ₂ (DMF) ₂	37.76
4	MOF-808-P_150C	-	39.40 ± 0.7

2. Catalytic Experiments

2.1. Recycle Test

For the recycling test, the catalyst was collected via centrifugation (3000 rpm, 10 min after reaction and thoroughly washed with ethanol and isopropyl alcohol (IPA) four times (3000 rpm, 15 min). The recovered catalyst was reactivated first at 60 °C and overnight at 150 °C. Reaction solution was adjusted to account for the catalyst loss (10–20 %). In the first recycle run, cinnamyl alcohol and carvone yield decrease with 25 %.

2.2. Reflux

For the reaction under reflux, 20 mg of activated MOF-808-P, 3.3 mL IPA, 145 μ L tetradecane, and 180 μ L *R*-carvone were placed in a 50 mL two-mounted flask connected to a condenser. The reaction mixture was refluxed at 80 °C and stirred at 250 rpm, while a N₂-flow was passed over the mixture to remove the formed acetone.

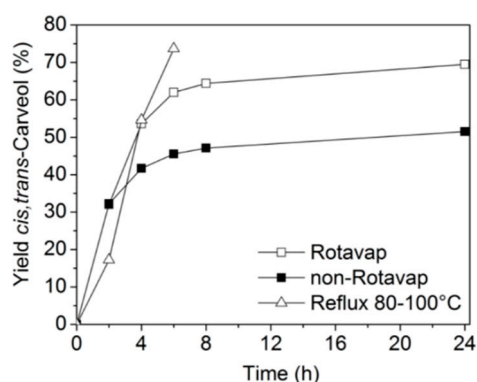


Figure S5. Evaporation of acetone and isopropanol and addition of fresh isopropyl alcohol (IPA) solvent (\square) indicate that the equilibrium of the Meerwein–Ponndorf–Verley (MPV) reduction of *R*-carvone with MOF-808-P can be shifted towards *cis,trans*-carveol. By performing the reaction under reflux at 80 to 100 °C, yield could be increased to 74 %.

2.3. 1-Indanol as Reducing Agent

MPV reduction reactions were carried out with 5 or 12 equivalents of IPA and 1-indanol in toluene.

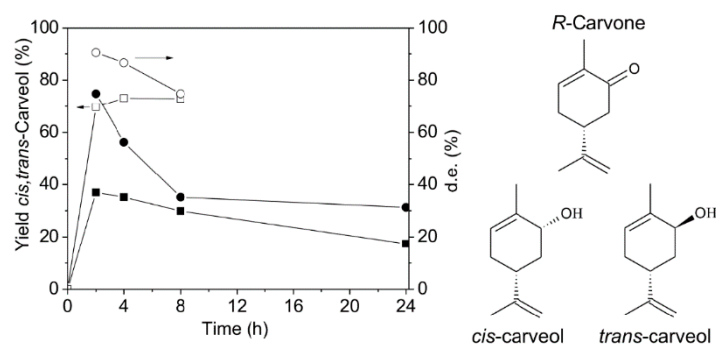


Figure S6. Meerwein–Ponndorf–Verley (MPV) reduction of *R*-carvone with MOF-808-P with 5 (filled) or 12 (open) equivalents of (*S*)-1-Indanol. When yield of *cis,trans*-carveol (\blacksquare, \square) reaches equilibrium (73 %), epimerization occurs and the diastereomeric excess (d.e., \bullet, \circ) decreases. (120 °C, Zr/substrate/reducing agent/toluene = 1/13/156/480).